10 p.

A Remark on the Configuration Interaction Approach*

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In 1928 Hylleraas[1] concluded that the expansion of the helium atom wavefunction in Legendre functions, $P_\ell(\omega)$, of the cosine of the angle between the r_1 and r_2 radius vectors is a relatively slowly converging series. The question was reopened in 1952 by Luke, Meyerott, and Clendenin[2] who thought they had obtained a rapid convergence with the first three terms ($\ell = 0,1,2$) of such an expansion for the 2^3S state of Li^+. Subsequent reassessments[3,4] have established beyond question that for the accuracy now possible, the procedure is slowly convergent. Nevertheless, there seems to be a continuing interest in the problem. Thus, Weiss[5] took the trouble to find the E^ℓ (the Legendre expansion for the wavefunctions leads to a corresponding series expression for the energy, $E = \Sigma_\ell E^\ell$) for the 1^1S ground state of helium for $\ell = 0,1,2,3,4$. Schwartz[6] has investigated a closely related problem in which the second-order perturbation energy coefficient, ϵ_2, is obtained by expanding the first-order wavefunction in the same sort of Legendre function expansion, so that ϵ_2 is obtained via $\epsilon_2 = \Sigma_\ell \epsilon_2^\ell$. His conclusion is that for ℓ large enough the ϵ_2^ℓ for the ground state should drop off as ℓ^{-4}. Schwartz also makes the guess that the energy series should converge as ℓ^{-6} for the triplet states as contrasted to the ℓ^{-4} convergence he expects for the singlets, and our results confirm this guess to some extent. Lakin[7], investigating the cause of the slow convergence, concludes that Weiss's argument that the slow convergence is due to the singularity at $r_{12} \to 0$ is not a sufficient explanation. Lakin

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bases some of his discussion on known E^{ℓ} values. And finally, Davis[8] has recently obtained E^0 for the 1^1S two-electron iso-electronic series through Z = 20 by a variational procedure. The perturbation procedure is a particularly convenient way to obtain the E^{ℓ} since to a large extent elaborate separate calculations, otherwise useless, are not necessary; by labeling the terms in the expansion set properly, it is possible to obtain the ϵ_{2n}^{ℓ} as mere incidentals in the calculation of the ϵ_{2n}. In addition, a single calculation suffices for an entire iso-electronic series. The individual E^{ℓ} are then obtained via $E^{\ell} = \Sigma_i Z^{2-i} \epsilon_i^{\ell}$. In Table I we present the ϵ_i^{ℓ} for i = 0,1,2,3 and ℓ = 0,1,2 for the 1^1S, 2^3S, 2^1P and 2^3P states of the two-electron iso-electronic series.[9] These results were obtained from our previous calculations on these systems[10]. We have also extended our previous calculations slightly to obtain ϵ_i^0 through i = 7 for the ground state. These latter, listed[9] in Table II, suffice to reproduce all of Davis's calculations satisfactorily, and, in fact, should give more accurate results from Z = 3 on. Indeed, if the extrapolation procedure, discussed elsewhere[10], is assumed valid here, then one or two additional significant figures can be estimated. For example E^0 to 7th-order for 1^1S helium is -2.87901453, but when extrapolated[11] comes to -2.8790274 in agreement with the value of Shull and Löwdin[4] (-2.87900 ± 0.00003) or of Davis[8] (-2.8790280 ± 0.0000018). Note from Table I the more rapid convergence of the series for the triplets than for the singlets. It is even possible that for triplet states a Legendre function expansion may be suitable if not too high accuracy is wanted.

Table I. The ϵ_i^{ℓ} in Atomic Units

State	ℓ	ϵ_0^{ℓ}	ϵ_1^{ℓ}	ϵ_2^{ℓ}	ϵ_3^{ℓ}
	0	-1.0	0.625	-0.12533198	-0.00521541
	1			-0.02644609	0.00805752
1^1S	2			-0.00361236	0.00315220
	$\epsilon_i - \epsilon_i^0 - \epsilon_i^1 - \epsilon_i^2$			-0.00227582	0.00270468
	0	-0.625	0.187928669...	-0.045317648	-0.007051597
	1			-0.001902139	0.001868871
2^3S	2			-0.000135301	0.000235263
	$\epsilon_i - \epsilon_i^0 - \epsilon_i^1 - \epsilon_i^2$			-0.000054104	0.000075621
	0	-0.625	0.259868922...	-0.14684854	-0.03760719
	1			-0.00780312	0.05580966
2^1P	2			-0.00091561	0.00348572
	$\epsilon_i - \epsilon_i^0 - \epsilon_i^1 - \epsilon_i^2$			-0.00145396	0.00443612
	0	-0.625	0.225727785...	-0.070480500	-0.019482739
	1			-0.002189892	0.002356303
2^3P	2			-0.000121887	0.000360426
	$\epsilon_i - \epsilon_i^0 - \epsilon_i^1 - \epsilon_i^2$			-0.000200324	0.000207490

Table II. The ϵ_i^0 for the 1^1S State in Atomic Units

i	ϵ_i^0	$\epsilon_i^0/\epsilon_{i-1}^0$
0	-1.0	
1	0.625	--
2	-0.12533198	--
3	-0.00521541	--
4	-0.00301007	.577
5	-0.00181567	.603
6	-0.00114702	.632
7	-0.00075762	.661

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9. Units of length a_0 ; units of energy 2Rhc.

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11. The ϵ_i^0 seem to be converging in the same fashion as the ϵ_i of reference 10. The exact behavior is not critical for the present purpose, and an analogous rate of convergence was assumed.